List of Actinide Projects

Past and Present

Project: Plutonium behavior in soils

Applicability: A study to measure adsorption of plutonium on INEEL soil materials. Relevant to current studies to select a site-specific Kd value for the RWMC.

Who: Scientists from Rocky Flats and Los Alamos

Miner, F. J., P. A. Evans, and W. L. Polzer, 1982, *Plutonium Behavior in the Soil/Water Environment Part I. Sorption of Plutonium by Soils*, RFP-2480, Rocky Flats Plant, Golden, CO.

When: 1982

Actinide(s): Plutonium

Tests: Batch adsorption experiments at three initial plutonium concentrations, and column studies where soil equilibrated with plutonium solution was added to the top of a column, and water passed through the column to elute the plutonium.

Materials: Thirteen soil samples from 7 DOE sites. Four of the samples were collected at the INEEL near an unspecified facility that handled plutonium. The soils were collected from 0-20 cm or at 40 cm depth (all near surface). The material is clay-loam to sandy-clay-loam. The characterization of the material as Polatis suggests surface soils near INTEC.

Test solutions: The test solution was deionized water with plutonium added as plutonium nitrate. The valence state was not determined or is not reported. pH was measured but not reported for batch experiments. pH is reported for a column experiment on INEEL soil and gives a pH range of 8.3 to 8.6.

Accomplishments: From batch adsorption experiments, the four soil K_d values showed a very broad range (Table 7). Column studies were also conducted with plutonium. They used a 4 cm long column and flushed plutonium through the column. For two INEEL soils, 99.5% and 93.9% of the plutonium remained in the first 1.3 cm of the column. For soil ID-B with a reported K_d of 144 ml/g, 1.8% of the plutonium was eluted from the column. For soil ID-A, with a reported K_d of 5,020 ml/g, less than 0.1% was eluted from the column. Observations of these investigators on the breakthrough of plutonium are interesting in light of more recent studies. In soil ID-B, there was a prompt pulse of plutonium occurring in the initial 20 ml eluent fraction of 0.9% of the original plutonium. The remaining effluent fractions contained continually decreasing amounts of plutonium. For sample ID-A there was no pulse of plutonium, but the concentration in the effluent fractions varied randomly between 0.001% and 0.004% of the original plutonium addition.

Current / Future Work: None

Material representative of SDA: Similar. Material varies from clay loam to sandy clay loam. Fine grained material is likely similar to fine grained materials at the SDA. The USGS has shown that INEEL sediment are derived from the same source area and show similar mineral characteristics. Surface material has not been subject to elevated temperature from subsequent basalt flows like interbed sediments.

Table 7 Plutonium Kd values measured on INEEL soils by Miner, Evans, and Polzer (1982).

Soil	Sample Depth (cm)	K_d (ml/g) Pu initial = 10^{-8} *M*	K_d (ml/g) Pu initial = 10^{-7} *M*	K_d (ml/g) Pu initial = 10^{-6} *M*	Avg. $K_d \pm 1\ \sigma$ (ml/g)
ID-A	40	1700	4300	5000	3,700 ± 1,700
ID-B	40	320	330	140	263 ± 107
ID-C	0-20	690	4100	4000	2,900 ± 1,900
ID-D	0-20	2100	1500	310	1,300 ± 900

Water chemistry representative of SDA: No. Water contained no inorganic or organic complexing agents representative of subsurface conditions at the SDA.

Project: Quantity and speciation of plutonium at INTEC

Applicability: An attempt to measure plutonium in Snake River Plain groundwater. Relevant to current attempt to monitor for actinides in groundwater at the RWMC. Relevant because oxidation state of plutonium in groundwater was determined.

Who: Jess Cleveland and T. Rees of the USGS

Rees, T. F., and J. M. Cleveland, 1983, *Characterization of Plutonium in Waters at Maxey Flats, Kentucky, and Near the Idaho Chemical Processing Plant, Idaho*, IAEA-SM-257/66, pp. 41-52.

When: 1980 to 1981

Actinide(s): plutonium

Tests: sampled ground water monitoring wells at INTEC in 1980 and 1981 close to the injection well while the well was injecting water containing an average of 1 pCi/L ^{238}Pu. Samples were filtered through 0.5 μm filters. Selective extraction of the samples to identify valence state.

Materials: natural groundwater. no solids involved.

Test Solutions: natural groundwater

Accomplishments: Plutonium was only detected in the well closest to the injection well (USGS-040, 700 ft from the injection well) at 0.066 pCi/L. The detection limit was 0.010 pCi/L. Samples were analyzed by alpha spectrometry. About 75% of the plutonium passed through the filter indicating a soluble form of plutonium. Found that virtually all of the plutonium was in the tetravalent form.

Current / Future Work: None

Materials representative of SDA: Not applicable

Water chemistry representative of SDA: Water chemistry of Snake River Plain aquifer is similar at INTEC and the RWMC.

Project: Speciation of plutonium and americium in RWMC groundwater

Applicability: Relevant to determining the empirical solubility of plutonium and americium in groundwater at the RWMC. Relevant to determining the oxidation state of plutonium in the groundwater at the RWMC

Who: Jess Cleveland and Ann Mullin of the USGS

Cleveland, J. M., and A. H. Mullin, 1993, *Speciation of Plutonium and Americium in Ground Waters from the Radioactive Waste Management Complex, Idaho National Engineering Laboratory, Idaho*, Water-Resources Investigations Report 93-4035, U. S. Geological Survey, Denver, CO.

When: 1993

Actinide(s): plutonium and americium

Tests: Investigators added plutonium and americium to natural groundwater and perched water collected at the RWMC.

Materials: No solids were used.

Test Solutions: Natural groundwater and perched water from the RWMC

Accomplishments: When Pu(V+VI) was added to containers of groundwater, no reduction to Pu(III) or Pu(IV) took place and essentially all of the plutonium remained in solution. When reduced plutonium [Pu(III+IV)] was added to ground water, appreciable precipitation occurred removing 50% or more of the added plutonium. From 67% to 98% of americium added to groundwater was removed from solution in groundwater from around the RWMC in 30 days. The solubility of americium in water from well 92 was the least of all the waters studied.

Current / Future Work: None

Materials representative of SDA: No solids used, not applicable.

Water chemistry representative of SDA: Directly. Water samples collected from groundwater and perched zone wells at the RWMC.

Project: Column studies of actinide migration through basalt and RWMC sediments

Applicability: Measurements of site-specific Kd values were made on material collected from the RWMC. Results are applicable to average site-specific conditions at the RWMC.

Who: Joint project at the INEEL and at Clemson University.

Newman, M. E., Indrek Porro, Rick Scott, F. M. Dunnivant, R. W. Goff, M. D. Blevins, S. M. Ince, John D. Leyba, T. A. DeVol, A. W. Elzerman, and R. A. Fjeld, 1996, *Evaluation of the Mobility of Am, Cs, Co, Pu, Sr, and U through INEL Basalt and Interbed Materials: Summary Report of the INEL/Clemson University Laboratory Studies*, ER-WAG7-82, INEL-95/282, Idaho National Engineering Laboratory, Idaho Falls, ID.

When: 1993 to 1995

Actinide(s): uranium, plutonium, and americium

Tests: Conducted batch Kd tests and column elution tests on crushed basalt and sediments.

Materials: Crushed basalt from the INEEL. Took nine sedimentary interbed samples from the vicinity of the RWMC and composited the material into one sample. All interbed sediment tests were conducted on this "composite" interbed material.

Test Solutions: Synthetic groundwater made up to have a similar composition to groundwater in the aquifer under the RWMC.

Accomplishments: Uranium transport is reasonably well explained by a K_d type model, with about 100% recovery in column tests on basalt. Retardation was about 2 for uranium. Plutonium and americium showed an enhanced mobility fraction of about 2% with a retardation factor of about 2 for crushed basalt columns. The remaining 98% of the plutonium and americium did not emerge from the column indicating retardation exceeded 200.

In packed interbed sediments, uranium transport through the column again showed simple transport behavior with 90% to 100% recovery of tracer. Retardation ranged from 30 to 43. Plutonium and americium showed a very small fraction of enhanced transport, with the bulk (>99%) of the Pu and Am remaining in the column with retardation > 200. Oxidation state determinations on plutonium in batch experiments showed that when the solid to liquid ratio in experiments was high, Pu(V) and Pu(VI) were reduced to Pu(IV).

Current / Future Work: None, in the mid 1990's, the INEEL group associated with this work left the laboratory, and there was no in-house group to continue the work. Work continued at Clemson University as discussed in the next section.

Materials representative of SDA: Directly, basalt and sediment samples collected from the vicinity of the SDA. Used composite materials, so values obtained reflect averages for subsurface materials.

Water chemistry representative of SDA: Directly, water used in experiments was a synthetic groundwater based on water samples from the vicinity of the SDA.

Table 8 Summary of batch and column measurements of Kd from Newman et al. (1996)

Isotope	Media	Batch K_d (ml/g)	Column K_d (ml/g)	Enhanced mobility K_d (ml/g)
Am	Basalt	70 to 280	> 60[1]	0.2
Am	Interbed	450 to 1100	> 48[1]	Present[2]
Pu(V)	Basalt	70 to 130		
Pu(V)	Interbed	5100 to 7900		
Pu(V)	Surface soil	7800 to 22000		
Pu(VI)	Basalt	12 to 24		
Pu(VI)	Interbed	110 to 690		
Pu(VI)	Surface Soil	1800 to 4900		
Pu(total)	Basalt		> 60[1]	.25
Pu(total)	Interbed		> 48[1]	Present[2]
U	Basalt	4 to 6	0.2 to 0.3	Not present
U	Interbed	3 to 6	7 to 10	Not present

1. Breakthrough did not occur, and so it is only known that the K_d is greater than the reported value.
2. An enhanced mobility fraction was present, but at too small a concentration to quantify a K_d.

Project: Column studies of actinide migration in RWMC interbed sediment

Applicability: Measurement of transport properties for actinides on material collected from the SDA. Results applicable to average conditions at the RWMC.

Who: Clemson University

Fjeld, R. A., J. T. Coates, and A. W. Elzerman, 2000, *Column Tests to Study the Transport of Plutonium and other Radionuclides in Sedimentary Interbed at INEEL*, Department of Environmental Engineering and Science, Clemson University, Clemson, SC.

When: 1995 to 2000

Actinide(s): thorium, uranium, neptunium, plutonium and americium

Tests: Column experiments measuring breakthrough

Materials: Used a composite RWMC interbed material

Test Solutions: synthetic groundwater

Accomplishments: Trivalent and quatravalent actinides, americium (III), thorium (IV), and plutonium (IV) were found to have a very small (< 0.01%) fast fraction with a retardation factor between 1 and 6 and a K_d less than 0.5. Americium (III) and plutonium (IV) showed a continuous small breakthrough during the experiment. However, 99.9% of the americium (III), 98.8% of the plutonium (IV) and 99.9% of the thorium (IV) were retained in the columns with a $K_d > 250$ ml/g. Plutonium (V) showed the same behavior as plutonium (IV), with a small fraction being released from the column with little retardation, and the bulk (99.8%) of the plutonium (V) remaining in the column.

Neptunium will be present in the ground in the neptunium (V) valence state. About half of the neptunium migrated through the columns with a retardation factor of 100 and a K_d of 25 ml/g. The other half of the neptunium did not emerge from the column. Fjeld and coworkers hypothesized that some of the neptunium was being reduced from the +V to the +IV valence state in the column. A column was oxidized with hydrogen peroxide, and a breakthrough test repeated. All of the neptunium was recovered, indicating that reduction was a factor in neptunium transport. A similar experiment with plutonium (V) did not result in breakthrough of plutonium. Reduction of plutonium in the soil is strong enough, that even after treatment of the soil with hydrogen peroxide, the soil can reduce plutonium (V) to plutonium (IV).

Uranium (VI) was used in testing. Uranium (IV) can be expected to act the same way the other quatravalent actinides act in the columns. Hexavalent uranium was completely recovered from the columns with a retardation factor of 3.2 to 8.2 and a K_d from 0.54 to 1.8. Experiments with water chemistry composition showed that complexing of uranium with carbonate ion was a very important factor in the transport of uranium. When carbonate ion was removed from the synthetic groundwater, the retardation factor jumped to 560 to 690 and the K_d jumped to 140 to 170 ml/g.

Complexing with organic complexing agents was also found to appreciably enhance migration of actinides. Quatravalent actinides were not mobile in the absence of complexing agents. When EDTA was added to test solutions, from 27% to 61% of the quatravalent actinide became mobile with retardation factors from 16 to 79 and K_d values from 4 to 19 ml/g. The presence of these agents could have a profound affect on the mobility of actinides.

Table 9 Summary of batch and column measurements of Kd from Fjeld, Coates, and Elzerman (2000)

Element	Special test conditions	Column retardation factor	Column K_d (ml/g)	Fraction of initial spike retained in the column	Enhanced mobility (fraction released / pore volume)	Effective K_d of enhanced mobility fraction (ml/g)
Am		>1000	> 250[1]	0.999	7.9e-5	4.5
Am	w/EDTA[3]	16	4	0.50	7.7e-5	continuous[2]
Th		>1000	>250	0.999	2.6e-5	continuous
Th	w/EDTA	23	5.75	0.73	2.3e-5	continuous
Pu(IV)		>1000	>250	.98	6.2e-6	continuous
Pu(IV)	w/EDTA	35 to 79	8.8 to 20	0.42	1.7e-4	continuous
Pu(V)		>1000	>250	.999	1.7e-4	continuous
Pu(V)	w/EDTA	>1000	>250	.999	3.6e-5	continuous
Pu(V)	oxidized sediment[4]	>1000	>250	.999	Not determined	
Np		97 to 156	24 to 39	0.32 to 0.60	1.5e-4	0.3 to 0.9
Np	w/EDTA	58 to 80	14.5 to 20	0.33 to 0.43	1.5e-4	0.6
Np	no carbonate[5]	195 to 310	49 to 78	0.19 to 0.33	Not present	na
Np	oxidized sediment	265 to 434	66 to 108	~0	Not present	na
U		3.2 to 8.2	0.8 to 2.0	0.04 to 0.08	Not present	na
U	w/EDTA	Not tested				
U	no carbonate	340	85	0.55	1.3e-4	3

1. Breakthrough did not occur, and so it is only known that the K_d is greater than the reported value.
2. An enhanced mobility fraction was present, but release was more or less continuous, not as a discrete peak
3. Simulated perched water with EDTA added.
4. Hydrogen peroxide was used to oxidize the sediment column before the test
5. Carbonate was left out of the recipe when the simulated perched water was mixed

Current / Future Work: No future work planned

Materials representative of SDA: Yes, composite of sedimentary interbed samples at the SDA. Representative of average conditions. Does not provide spatial distribution or information on variability.

Water chemistry representative of SDA: Yes, water chemistry of aquifer. Generally representative of low TDS water in the subsurface at the SDA.

Project: Measurement of adsorption isotherms on RWMC interbed samples

Applicability: Adsorption isotherms were measured using five concentrations of uranium and neptunium on RWMC interbed sediments. Results give information on variability of adsorption on interbed materials. Results can be used directly in TETRAD to simulate transport.

Who: Clemson University

Results not published

When: Fall 2000

Actinide(s): Uranium and neptunium. Attempts were made to measure isotherms for americium and plutonium, but Am and Pu could not be kept in solution in the simulated groundwater. Without a dissolved aqueous phase, a liquid solid partitioning coefficient could not be measured.

Tests: Batch adsorption experiments at five concentrations of actinide

Materials: Fourteen samples collected from wells drilled at the SDA (Inside and Outside well series) in 2000. Samples are from the 110-ft interbed and the 240-ft interbed.

Test Solutions: Synthetic RWMC groundwater

Accomplishments: There was some money left over in the contract in late calendar year 2000, so a quick investigation was initiated to measure adsorption isotherms on interbed sediments from the SDA. Fourteen interbed samples were sent to Clemson for analysis. Isotherms were measured for uranium and neptunium. When preparing test solutions for batch experiments with plutonium and americium, researchers could not keep the tracers in solution. The plutonium and americium formed particles in solution. A valid liquid-solid partition coefficient cannot be obtained if the tracer is not in solution to begin with. No isotherms were measured for plutonium and americium.

For neptunium and uranium, isotherms showed distinct nonlinearity. A good fit to both actinides was obtained using a Freundlich isotherm. The K values of the Freundlich isotherm showed a large amount of variation, but the exponents of the isotherms were very similar for all samples (**Table 10**). Some, but not all, of the soil samples sent to Clemson for isotherm analysis were also sent to Southwest Research Institute for determination of material properties that might affect adsorption. The contract with Clemson is ended, and no additional work is planned with Clemson at this time.

Current / Future Work: No additional work planned at this time.

Materials representative of SDA: Directly. Samples of interbed material were collected from wells drilled inside and adjacent to the boundaries of the SDA. Individual samples were tested so information on variability was obtained.

Water chemistry representative of SDA: Yes, water chemistry of aquifer. Generally representative of low TDS water in the subsurface at the SDA.

Table 10 Freundlich and linear isotherm parameters for neptunium and uranium, measured at Clemson University.

Sample ID	Neptunium Freundlich K	Neptunium Freundlich n	Neptunium Kd (ml/g)	Uranium Freundlich K	Uranium Freundlich n	Uranium Kd (ml/g)
7DS00101KD	245.74	0.59	99.96	73.77	0.81	36.90
7DS00301KD	90.62	0.62	27.15	53.49	0.78	21.47
7DS00901KD	99.54	0.59	24.59	17.31	0.78	5.90
7DS00701KD	23.96	0.65	5.93	45.68	0.76	16.30
7DS00501KD	155.44	0.56	37.35	37.21	0.81	16.51
7DS01701KD	133.17	0.56	33.86	40.09	0.77	14.33
7DS02301KD	109.03	0.56	27.89	34.78	0.81	15.42
I2S-INEEL-105	51.96	0.65	15.06	40.02	0.78	15.44
I1S-INEEL-109	279.87	0.58	97.50	34.83	0.78	12.73
I4D-INEEL-234	86.09	0.54	15.66	22.88	0.76	7.30
I4D-INEEL-231	123.71	0.53	26.51	32.50	0.76	10.54
I1D-INEEL-234	95.02	0.60	25.44	39.56	0.87	21.70
I4D-INEEL-224	162.28	0.54	40.69	31.07	0.81	13.27
I3D-INEEL-229	255.86	0.57	84.53	27.49	0.77	9.34

Project: Site specific partition coefficients for actinides in RWMC sedimentary interbed material

Up until the fall of 2000, all of the experimental work at Clemson was done with a composite interbed material. No information had been gathered on the spatial distribution of adsorption parameters. In addition, a review of the OU 7-13/14 interim risk assessment by the U. S. Geological Survey (USGS 1999), water chemistry was identified as a potential issue affecting partitioning. In the summer of 2000, a study was begun at the INEEL as a joint effort of the Geosciences Department and the Radioanalytical Laboratory at INTEC to study the spatial distribution of partition coefficients.

Applicability: Results will provide information on variability of Kd for interbed materials. Analysis of correlation between Kd and material properties will test hypotheses about what material properties affect sorption. Variation in Kd that can be explained by material properties will allow reduction of variance in Kd, and a better prediction of migration for risk assessment. Comparison of results from high TDS water will allow assessment of the effects of water chemistry on transport. May support conclusions concerning the conservatism of selected Kd values.

Who: Partition coefficients to be measured at the Radioanalytical Lab at INTEC, soil material properties measured at Southwest Research Institute

Hull, L. C., M. N. Pace, and T. J. Tranter, 2000, *Test Plan to Measure Adsorption of Actinides on Interbed Materials from the Radioactive Waste Management Complex*, DOE/ID-10796, U. S. Department of Energy, Idaho Falls, ID.

When: Soil materials measured in Sept of 2000. Partition coefficients planned to be measured in March of 2001. Independent Hazard Review is complete. Work is pending a CX determination on a NEPA Environmental Checklist.

Actinide(s): Uranium, neptunium, plutonium, americium

Tests: Batch adsorption experiments at one concentration in a high TDS water found under the eastern end of the SDA. Samples were sent to Southwest Research Institute for characterization of material properties (surface area, extractable oxides, cation exchange capacity, and bulk and clay mineralogy).

Materials: Twenty four samples of interbed material from discrete intervals in wells drilled adjacent to the SDA were selected from the 110-ft and 240-ft interbeds.

Test Solutions: A high TDS water found in lysimeters in well TW-1. This water has high chloride concentrations from the magnesium-chloride brine that was applied to the roads in the SDA.

Accomplishments: A test plan was prepared (Hull, Pace, and Tranter 2000) to develop information on spatial variability in K_d values, to attempt to correlate the K_d measurement to other material properties, and to address the effect of water chemistry. Material property results have been received from the laboratory. Samples were analyzed for bulk and clay mineralogy, surface area, cation exchange capacity, and extractable oxides of iron, manganese, aluminum, and silica.

Current / Future Work: In the next 90 days, expect to measure partition coefficients for the high TDS water.

Materials representative of SDA: Samples were collected from sedimentary interbeds at the SDA.

Water chemistry representative of SDA: Water is representative of the high TDS water under the eastern end of the SDA.

Project: Uranium roaster oxide dissolution / solubility

This project is still under development. An experiment is planned to measure the rate of dissolution of this oxide in water and to determine what happens to the uranium over time in water. This information will be used in the source term model for the risk assessment.

Applicability: Release of uranium from the waste will be based on a model that includes solubility. This task will measure the solubility of uranium oxide waste from the Rocky Flats Plant to verify computer models of solubility. Results are directly applicable to the source term model for risk assessment.

Who: Work will be done at the Radioanalytical Lab at INTEC.

Dicke, C. A., and K. J. Holdren, 2001, *Sampling and Analysis Plan for Characterization and Leaching Studies of Depleted Uranium from the Rocky Flats Plant (DRAFT)*, INEEL/EXT-2000-01434, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID.

When: Spring or summer 2001.

Actinide(s): uranium

Tests: batch dissolution tests

Materials: A sample of uranium roaster oxide has been found at the Rocky Flats Plant. This roaster oxide is from the period when waste was being shipped to the INEEL for disposal.

Test Solutions: Synthetic RWMC groundwater

Accomplishments: A draft workplan has been written and reviewed. Revisions are currently being made.

Current / Future Work: Craig Dicke, a subcontractor, is preparing the test plan (Dicke and Holdren 2001). The work is planned to take place at the INTEC Radioanalytical Laboratory. The test plan has just completed internal review and has been returned to Craig to address comment

Materials representative of SDA: Uranium material is from Rocky Flats and represents material buried at the SDA

Water chemistry representative of SDA: Since this is inside the waste, and we don't have any measurements of water chemistry within the waste, this will have to be estimated based on professional judgement.